



U.S. Department of Energy  
Office of Civilian Radioactive Waste Management



# The In-Drift Chemical Environment During the Above-Boiling Period

Presented to:  
**Nuclear Waste Technical Review Board**

Presented by:  
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# Acknowledgements

- **In-drift chemical environment**
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  - ◆ Tom Wolery, Lawrence Livermore National Laboratory
- **Dusts**
  - ◆ Zell Peterman, United States Geological Survey
  - ◆ Tom Wolery, Lawrence Livermore National Laboratory
- **THC and acid gas volatilization**
  - ◆ Nic Spycher, Lawrence Berkeley National Laboratory
  - ◆ Eric Sonnenthal, Lawrence Berkeley National Laboratory
  - ◆ Guoxiang Zhang, Lawrence Berkeley National Laboratory



# Overview of Presentation

- **Effect of Thermal-Hydrologic (TH) environment on in-drift chemistry during the above-boiling period**
- **A first look at salt deliquescence**
- **Salt minerals in dust in the repository**
  - Can they generate  $\text{CaCl}_2$  or  $\text{MgCl}_2$  brines?
- **Stability of salt minerals at temperature**
- **Acid gas volatilization from salt assemblages at temperature**
- **Another look at salt deliquescence**
  - How much water is absorbed?
  - What composition brines can develop?
- **Conclusions**



# Effect of TH Environment on In-Drift Chemistry During Above-Boiling Period

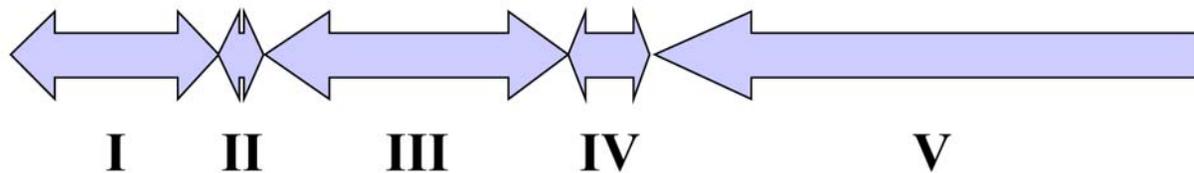
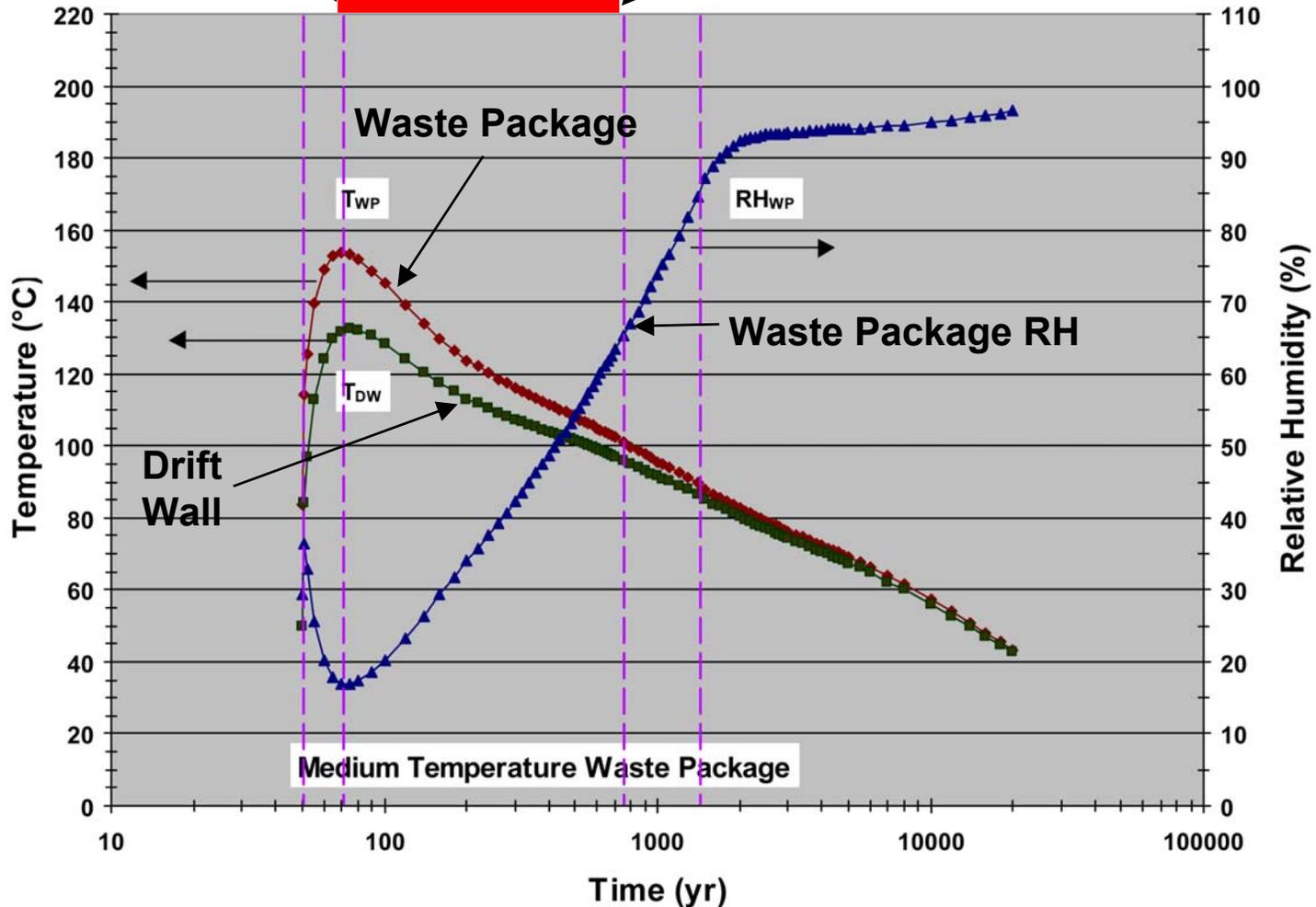


# In-Drift Chemical Environment During the Above-Boiling Period

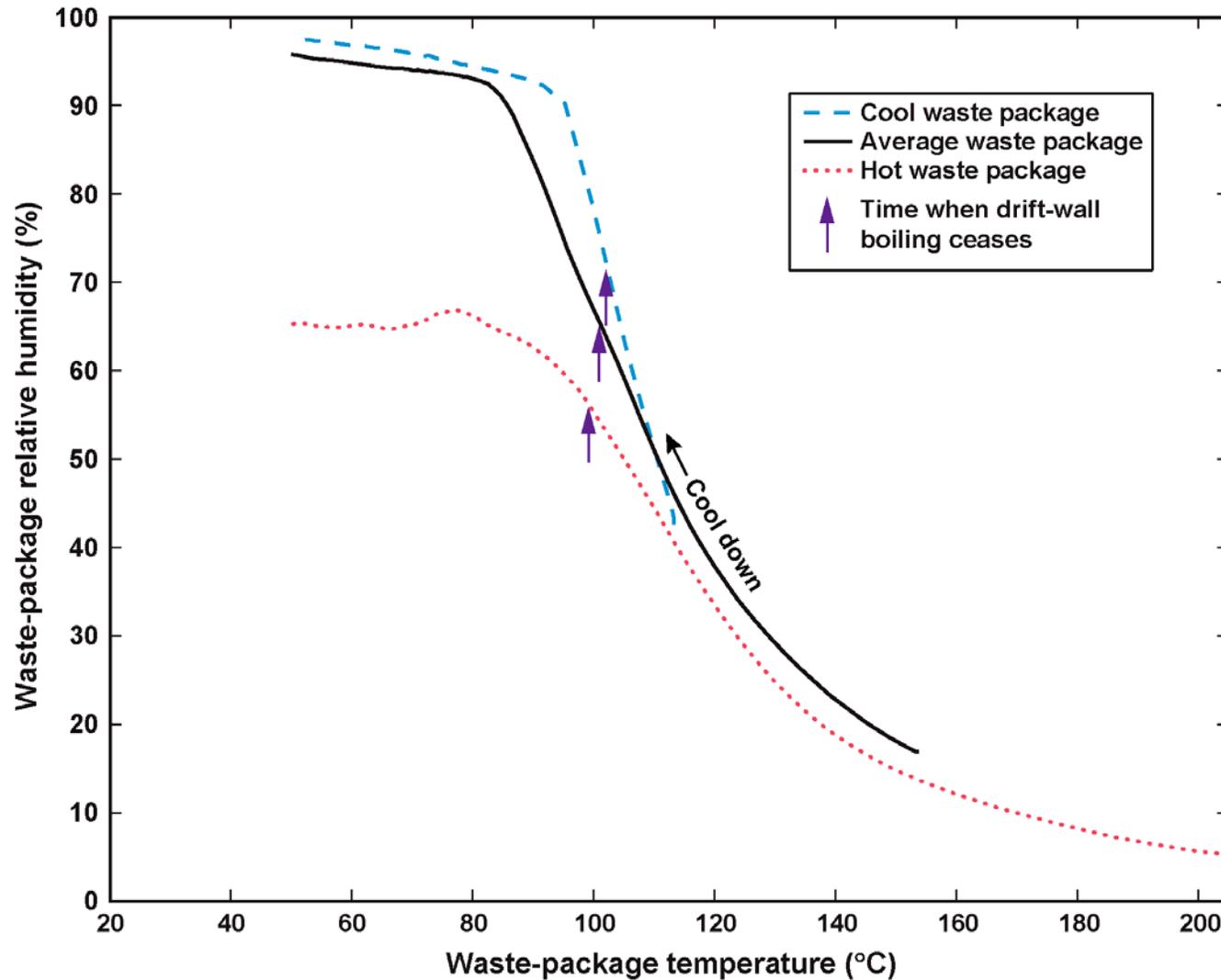
- **Focus on drift environment where drift wall temperatures are above boiling, which includes:**
  - **Relatively short heating period that dries out the drift and rock**
  - **Extended period in which drift wall gradually cools to boiling point—no seepage of water possible**
- **Issues during this period include:**
  - **Deliquescence of salt originating from dust accumulated on the waste package**
  - **Possible generation of acid gases from deliquescent salts and their fate in the drift environment**



# Above-Boiling Period



# T-RH Trajectories for Waste Packages



RHvsT\_cool\_3WPs



# Salt Deliquescence

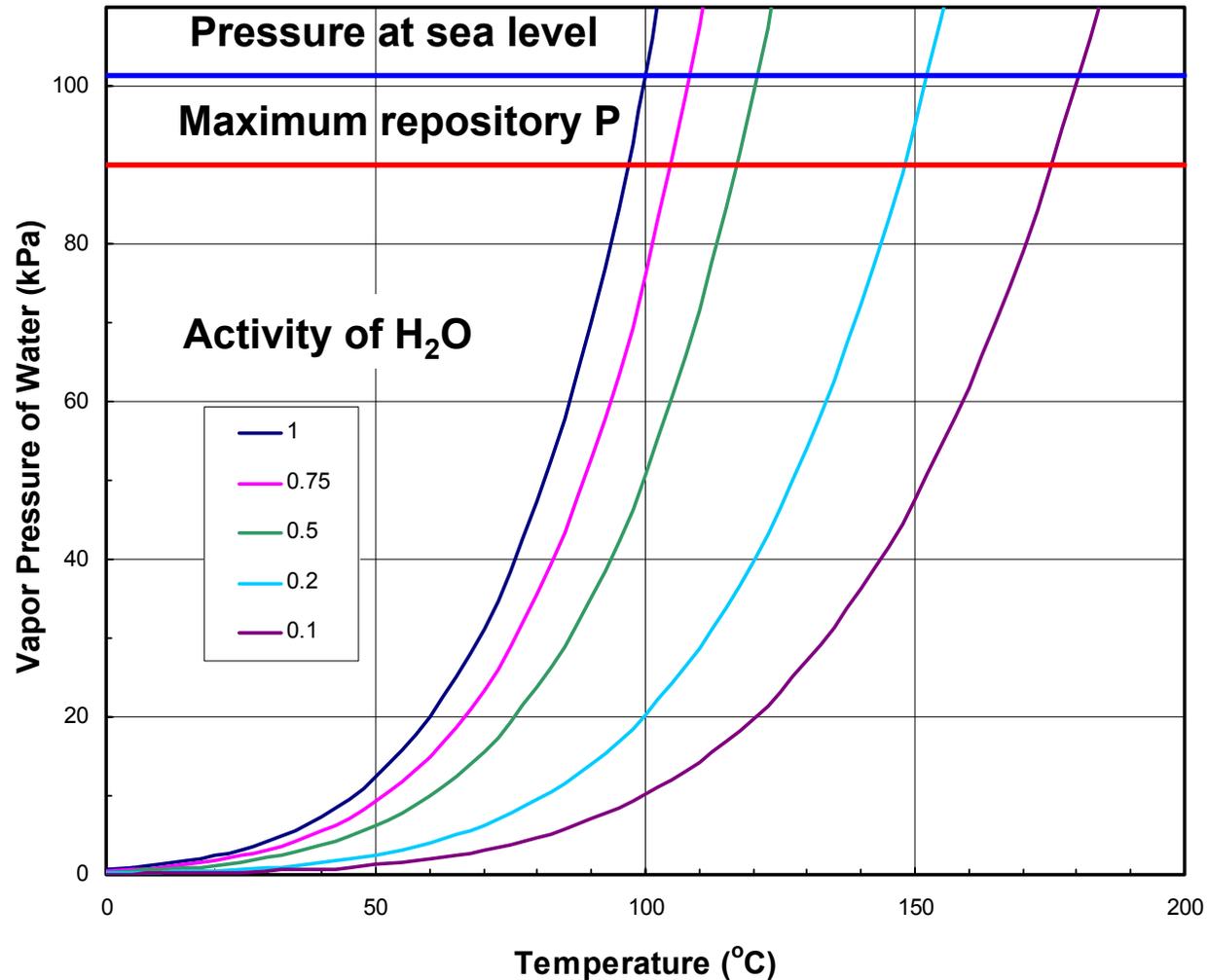


# A First Look at Salt Deliquescence

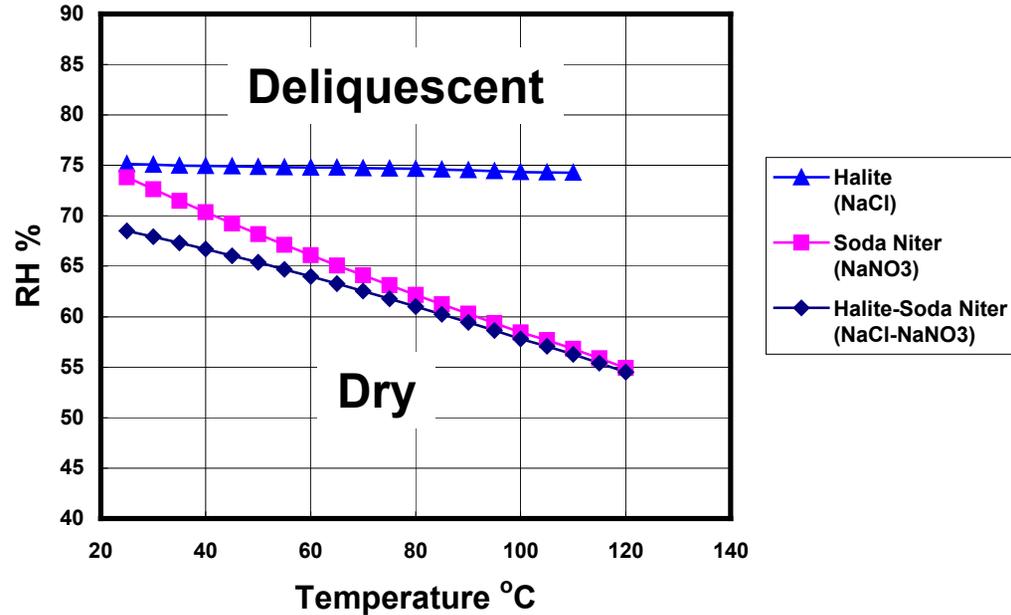
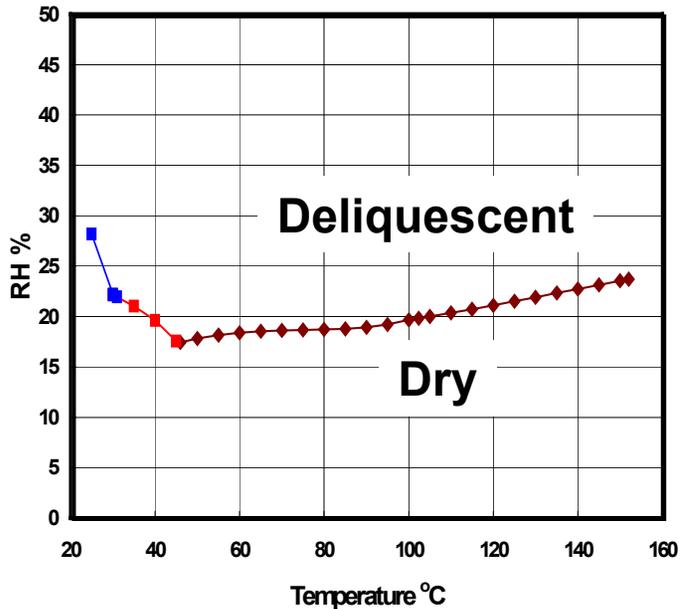
- **Dusts originating in the repository or brought in by ventilation may contain salts that deliquesce at a relative humidity (RH) < 100%**
- **What is salt deliquescence?**
  - **Activity of water (x 100) equates to RH**
  - **Activity of H<sub>2</sub>O in equilibrium with a saline brine is lower than 1 (pure water), so these brines will absorb H<sub>2</sub>O when RH (activity of H<sub>2</sub>O in atmosphere) > activity of H<sub>2</sub>O in brine**
  - **For highly deliquescent salts, a brine will exist above the boiling point of pure H<sub>2</sub>O (boiling point elevation)**



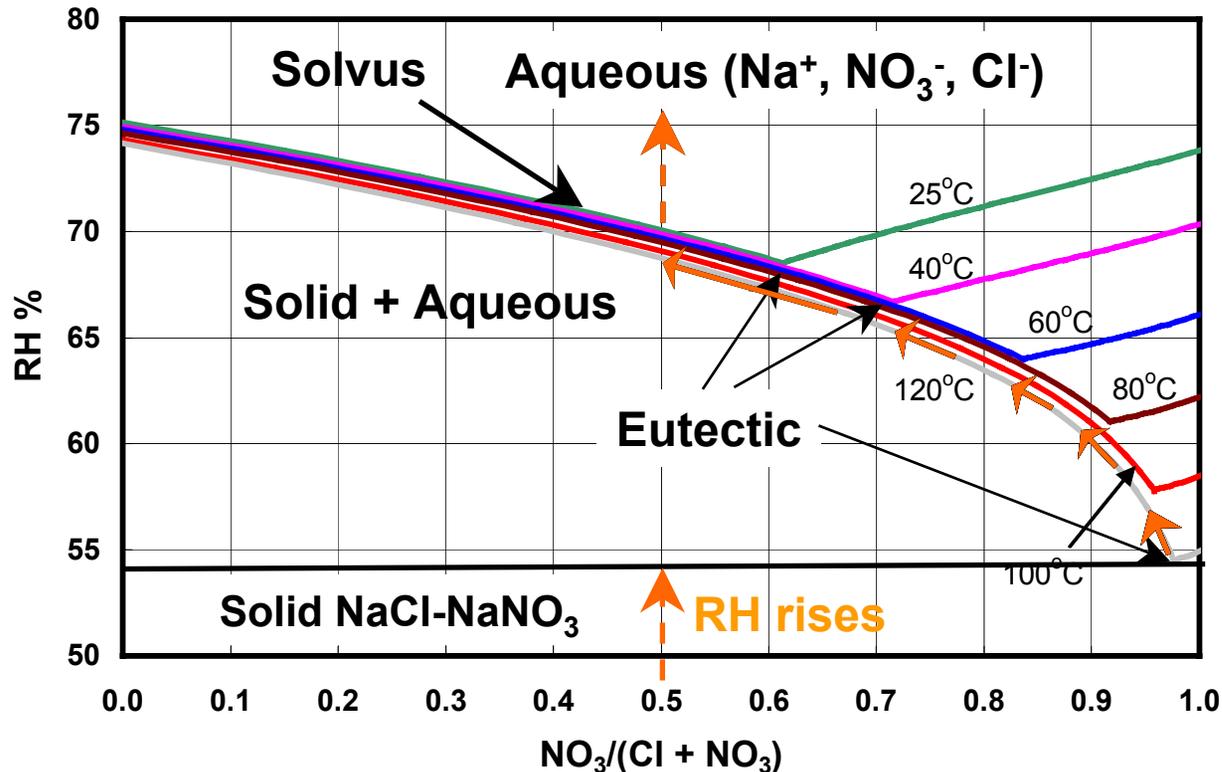
# Vapor Pressure of Water as a Function of Temperature and Activity of Water



# Deliquescence RH for Some Salts



# RH vs. Mole Fraction $\text{NO}_3$ for NaCl- $\text{NaNO}_3$ system



- As RH rises in the drift, eutectic for a salt or salt assemblage will be reached
- First aqueous solution to form will have eutectic composition
- A bulk composition different from the eutectic composition will cause aqueous solution to migrate along solvus



# Salt Minerals in Dust

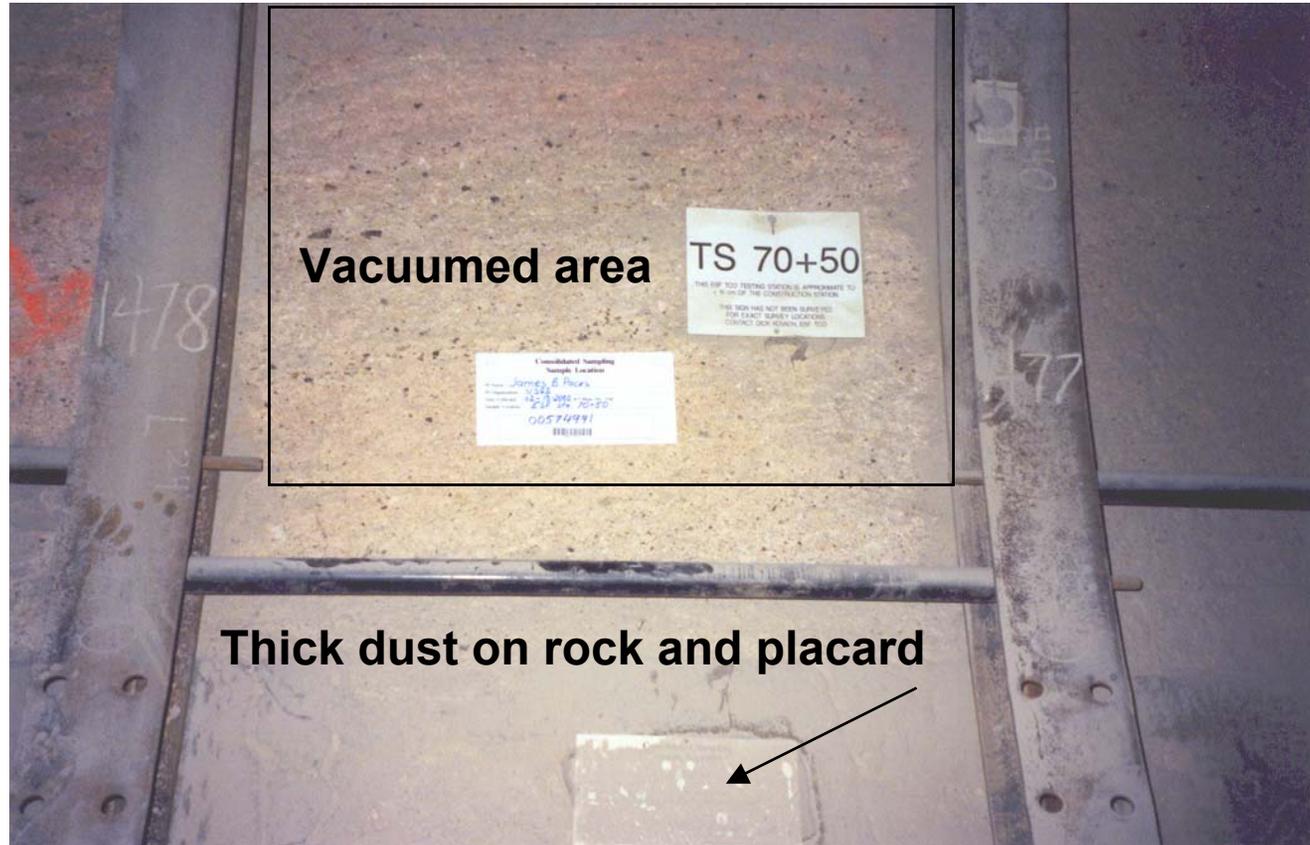


# Importance of Dusts during the Above-Boiling Period

- **Due to lack of seepage during the above-boiling period, salt-bearing dusts are the chief concern because of their potential for deliquescence**
- **Small amounts of soluble salts found in repository dust, higher amounts expected if atmospheric dust is more important**
- **Chief concern are chloride-bearing salts because of their potential for corrosion of the Alloy 22 waste packages in the repository**



# Dust Collection (Phase II) by United States Geological Survey



**Dust collected in Phase II by vacuuming surfaces. The amount of dust accumulation ranged from 0.012 to 0.023 gm/cm<sup>2</sup>**

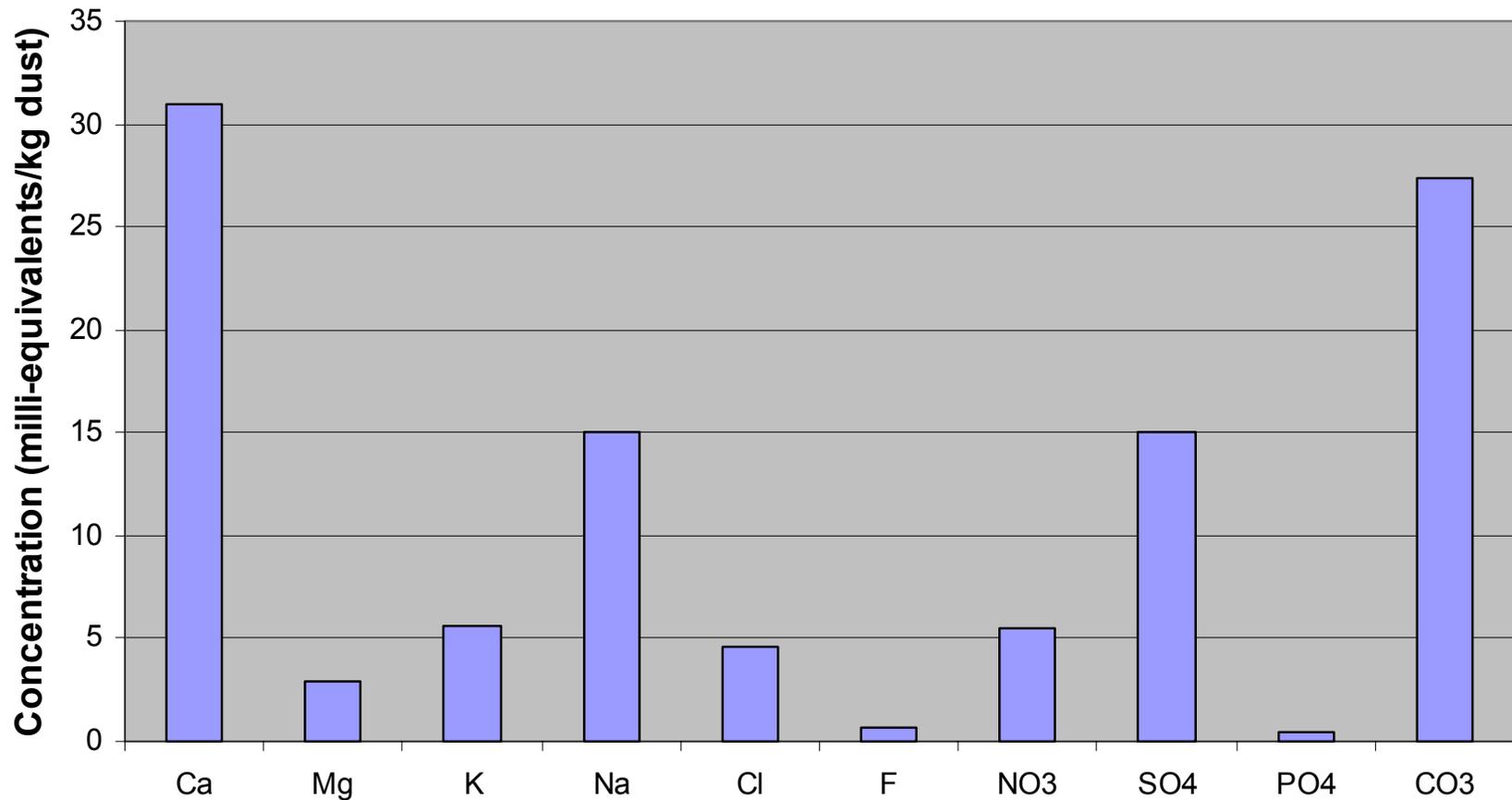


# Dust Analysis

- **Soluble content of dust analyzed by subjecting samples to a distilled water leach**
- **Evaporation of leachates yields salt minerals that can be identified**
- **Primary salt minerals calculated using an equilibrium/mass balance “evaporation” (EQ3/6)**



# Average of Soluble Cations and Anions



# X-Ray Diffraction Analyses of Salts from Evaporated Dust Leachate

X-ray diffraction analysis of salts precipitated from evaporated dust leachate

Salt	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
NaCl	X	XX	XX	XX	XX
KCl					
NH <sub>4</sub> Cl	X	X	X		
CaCO <sub>3</sub>		XX			
CaSO <sub>4</sub> 2H <sub>2</sub> O	XX	X		X	
CaSO <sub>4</sub> 5H <sub>2</sub> O			XX	X	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	X				
(NH <sub>4</sub> ,K)H <sub>2</sub> PO <sub>4</sub>	X				
CaC <sub>2</sub> O <sub>4</sub> 2H <sub>2</sub> O		X	X		

**XX** Major Component

**X** Minor Component

Analyses conducted at the United States Geological Survey



# Salt Mineralogy Calculated with EQ3/6

Dust leachate solutions are “evaporated” computationally with EQ3/6 to yield a primary assemblage of deliquescent salts

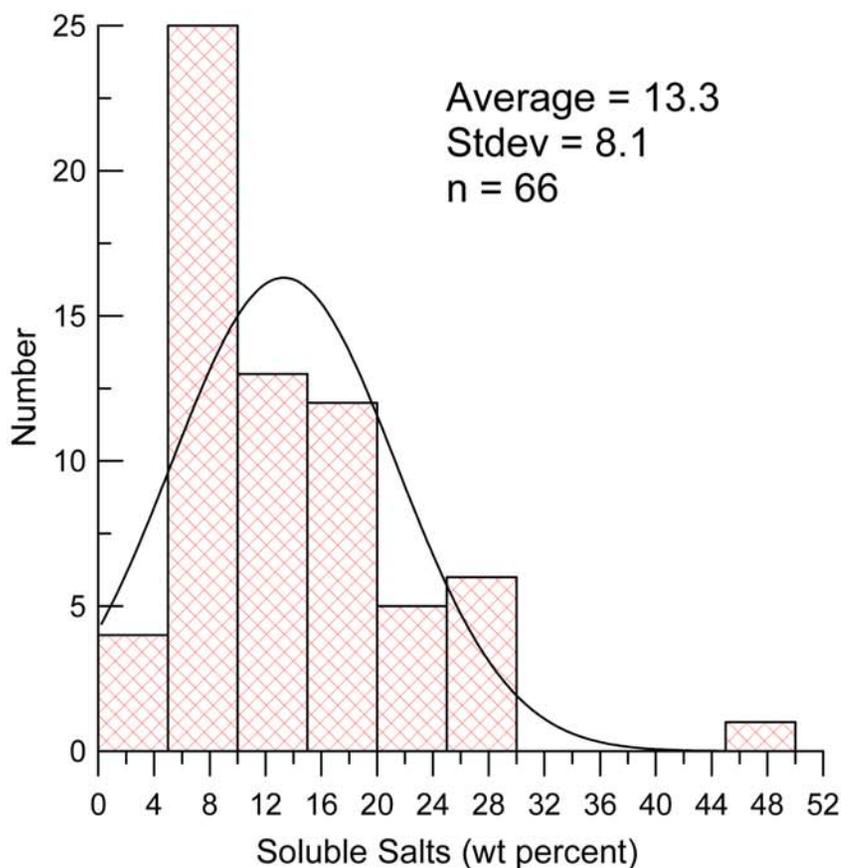
Main Predicted Salts	Occurrence %
NaCl-NaNO <sub>3</sub> -KNO <sub>3</sub> -KBr	28
NaCl-KNO <sub>3</sub> -KBr	68
Ca(NO <sub>3</sub> ) <sub>2</sub> -NaCl-NaNO <sub>3</sub> -KNO <sub>3</sub> -KBr	4

No CaCl<sub>2</sub> or MgCl<sub>2</sub> salts predicted

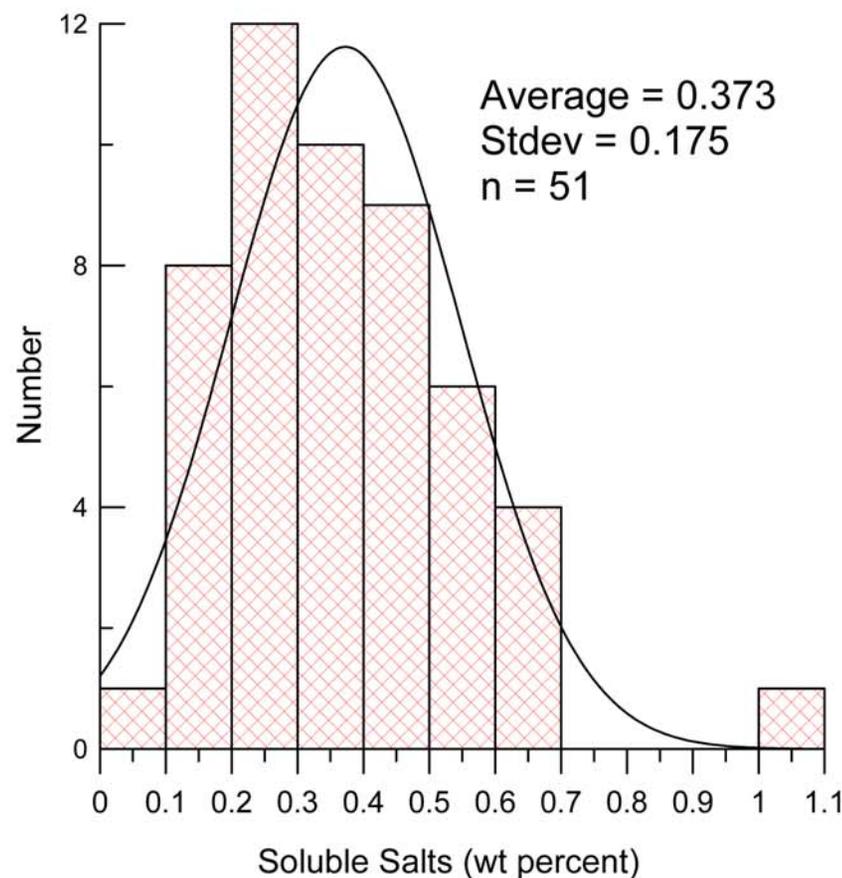


# Different Soluble Salt Contents in Atmospheric and ESF Dust

**Atmospheric Dust  
(Reheis, 2003)**



**ESF Dust  
(Peterman et al., 2003)**



# Can Salt in Dust Generate $\text{CaCl}_2$ Brines?

- A  $\text{CaCl}_2$  brine is possible only if the following conditions on the soluble salt fraction are both satisfied:
  - $\text{Ca} > \text{SO}_4 + \text{CO}_3$  ( $\text{CaSO}_4$  and  $\text{CaCO}_3$  are relatively insoluble)
  - $\text{Cl} > \text{Na} + \text{K}$  ( $\text{NaCl}$  and  $\text{KCl}$  will precipitate before  $\text{CaCl}_2$ )
- ~96% of the tunnel dusts fail to satisfy the first condition
- The remainder (~4%) satisfy the first condition, but not the second



# Can Salt in Dust Generate $\text{MgCl}_2$ Brines?

- The formation of an  $\text{MgCl}_2$  brine requires the following three conditions all be satisfied:
  - $\text{Mg} > \text{CO}_3$  ( $\text{MgCO}_3$  is relatively insoluble)
  - $\text{Cl} > \text{Na} + \text{K}$  ( $\text{NaCl}$  and  $\text{KCl}$  will precipitate before  $\text{MgCl}_2$ )
  - A “low silica” environment, since Mg is likely to be tied up by the silica in the soluble fraction
- These conditions do not occur in the repository



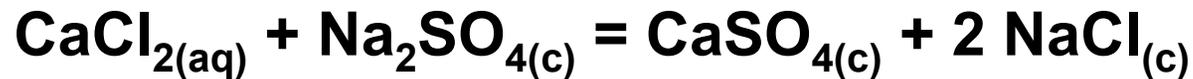
# The Presence of $\text{CaCl}_2$ or $\text{MgCl}_2$ Minerals in Outside Dust Is Very Unlikely

- The minerals are known to exist on the earth's surface at only a few places (e.g.,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  in Antarctica)
- The few known surface occurrences appear to be ephemeral
  - Very low RH conditions (<25%) required to preserve these salts in situ
  - Low RH conditions even harder to maintain during transport of salts



# Is Equilibrium Relevant for Salts in Dust?

- Salts in dust on the metal barrier surfaces may be a mechanical mixture and therefore not in thermodynamic equilibrium
- However, a disequilibrium salt assemblage would almost immediately equilibrate upon initial deliquescence, leading back to a dry state via a reaction such as:



- Experimental studies indicate reaction times on the order of 2 days or less
- The reaction products have higher Deliquescence RH points (causing them to dry out) because of their greater thermodynamic stability and lower solubility



# Soluble Ionic Ratios (mol/mol) Are Very Similar Among Tunnel Dusts and Nevada Rainfall

	Tunnel Dusts <sup>1</sup>			Nevada Rainfall <sup>2</sup>		
	P07	P14	P10	CA95	NV00	NV05
Na/Cl	2.699	4.069	2.894	2.070	1.127	1.828
K/Cl	1.221	1.528	1.237	0.158	0.139	0.207
NH <sub>4</sub> /Cl	N/A	N/A	N/A	2.605	5.514	4.633
Mg/Cl	0.072	0.305	0.175	0.336	0.555	0.417
Ca/Cl	8.472	6.389	2.348	3.101	2.973	2.907
NO <sub>3</sub> /Cl	4.002	1.671	0.776	2.969	5.146	3.839
SO <sub>4</sub> /Cl	3.123	3.293	1.458	1.009	1.384	1.555
CO <sub>3</sub> /Cl	4.839	4.737	2.057	2.860	2.461	2.683

<sup>1</sup>Three Phase I samples, each representing a different key salt assemblage

<sup>2</sup>National Atmospheric Deposition Program, 2002 Annual Mean Data  
(CA95=Death Valley, NV00=Red Rock, NV05=Great Basin)



# Stability of Salt Minerals at Temperature

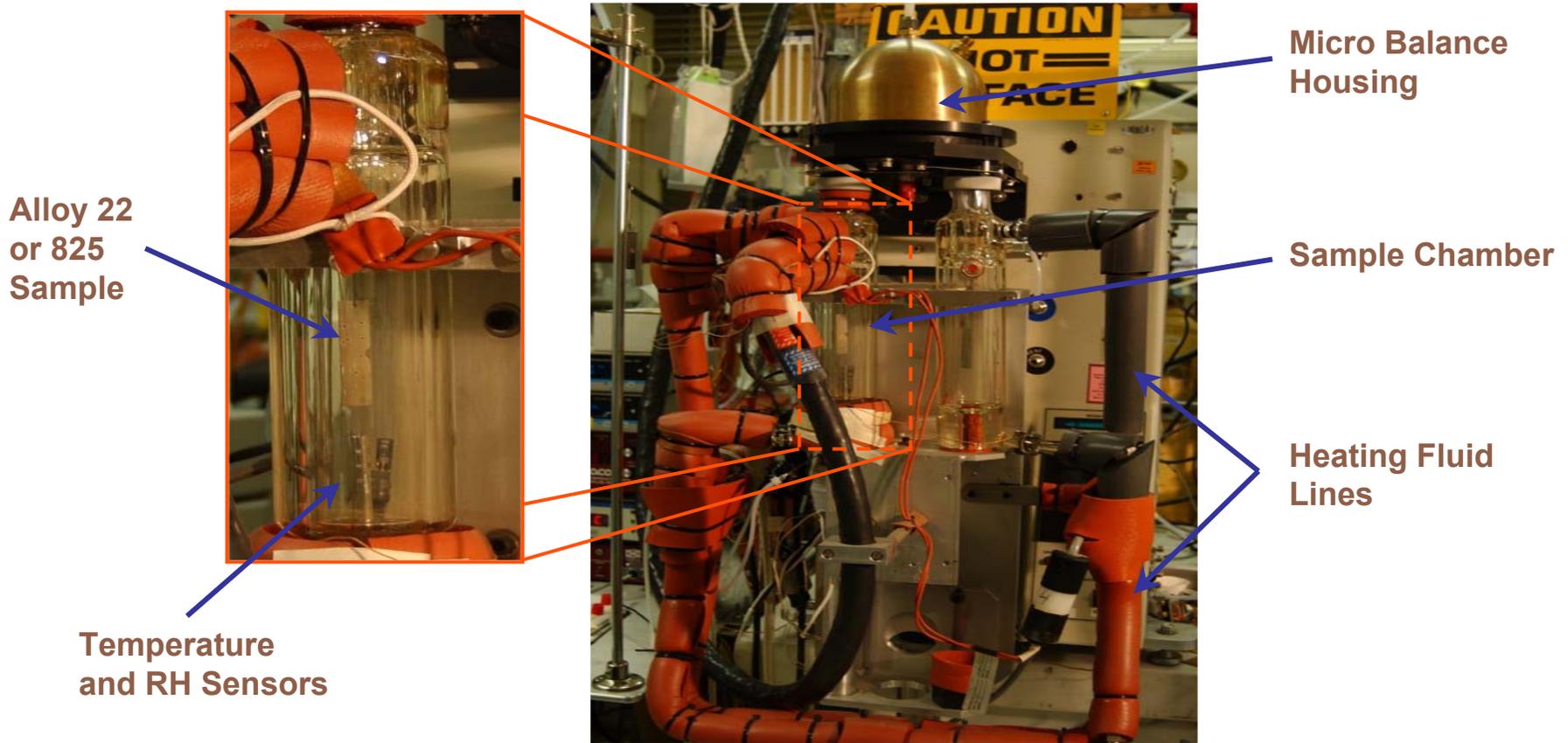


# Stability of $\text{CaCl}_2$ , $\text{MgCl}_2$ , and $\text{NaCl}$ Salts

- **Although not expected based on preceding arguments, the stability of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  has been evaluated experimentally**
- **Stability of  $\text{NaCl}$ , which is expected to be present in small amounts, has now been investigated experimentally**
- **Salt stability evaluated using thermogravimetric analysis (TGA) under controlled temperature and RH conditions at Lawrence Livermore National Laboratory**



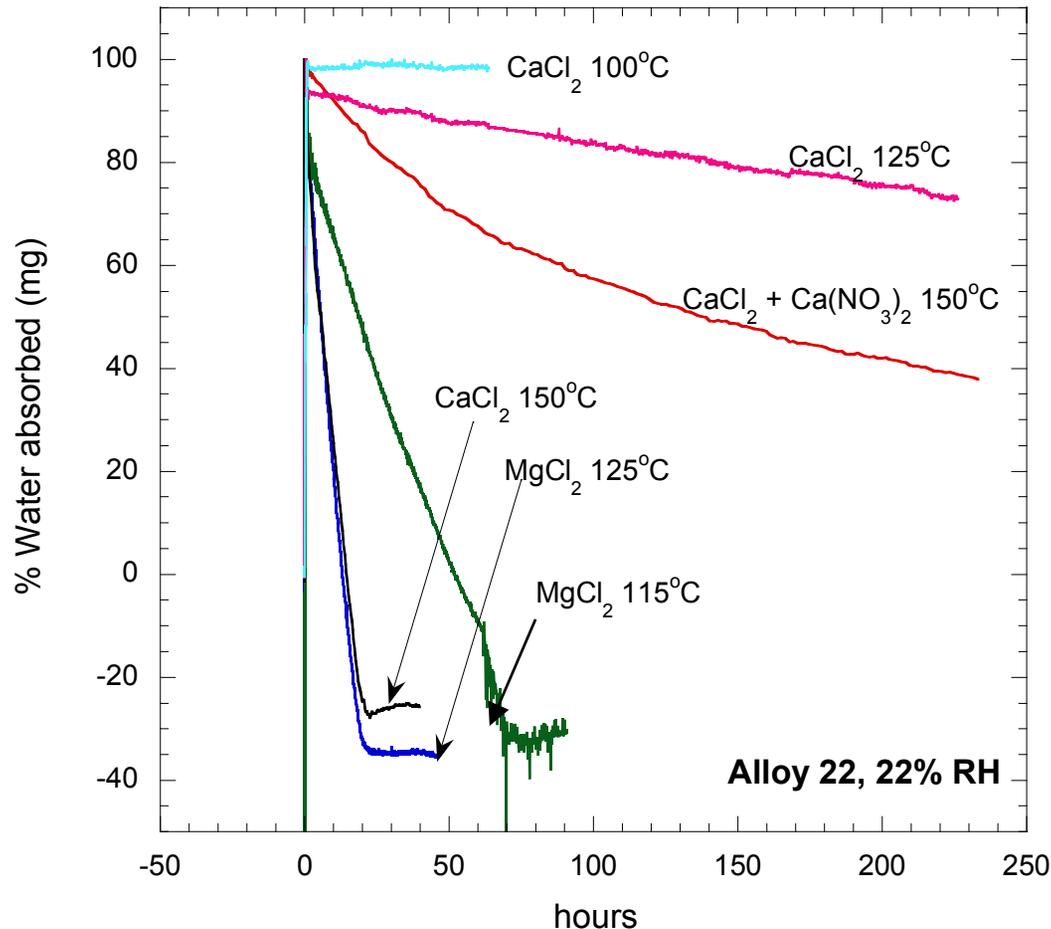
# Deliquescence Brines Studied with Thermogravimetric Analysis at LLNL



- Sensitive to weight changes as small as “tens of micrograms”
- Operation at temperatures up to 150°C



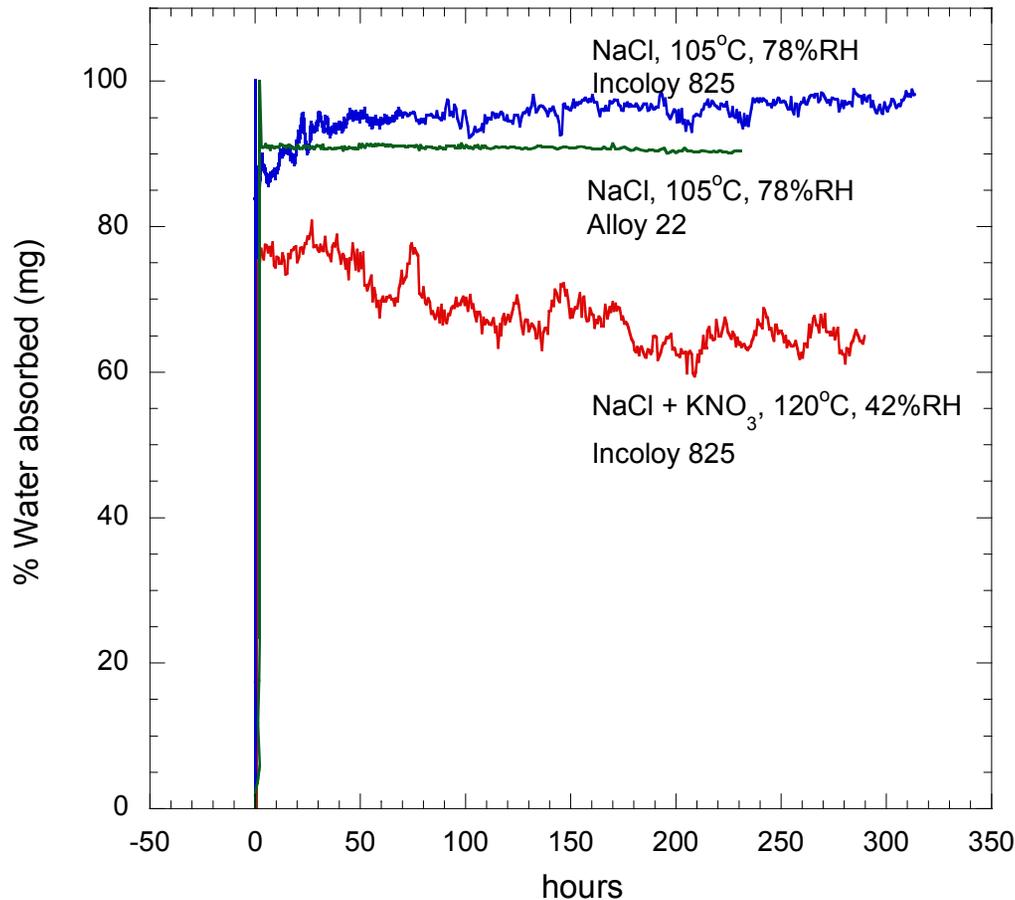
# Deliquescence and Stability of $\text{CaCl}_2$ and $\text{MgCl}_2$ Salts in TGA Experiments



- **100°C:  $\text{CaCl}_2$  aqueous films are stable for duration of test**
- **125°C:  $\text{CaCl}_2$  solution evolves slowly, forming insoluble precipitates**
- **150°C:  $\text{CaCl}_2$  solution evolves rapidly, forming insoluble precipitates and acid gas**
- **$\text{MgCl}_2$  transforms within hours at all temperatures, becoming non-deliquescent**



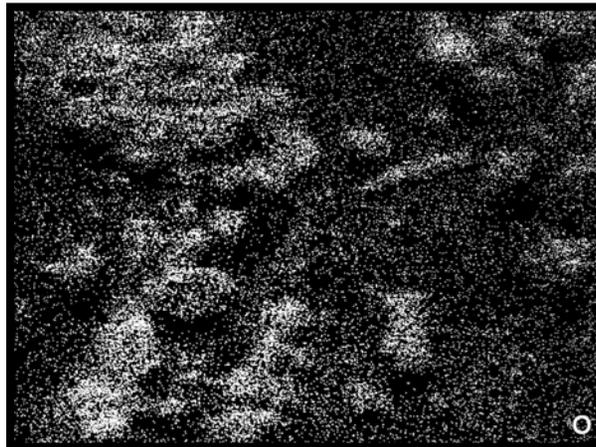
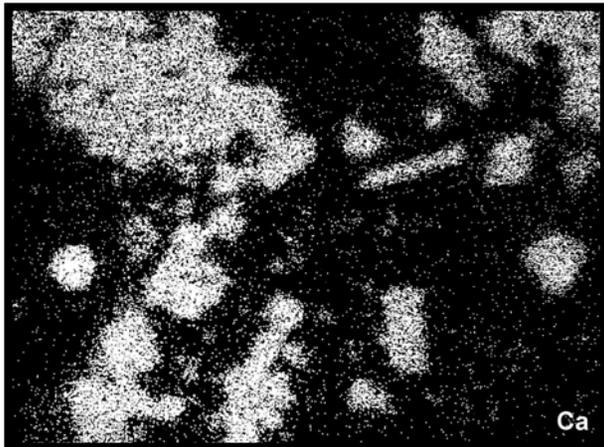
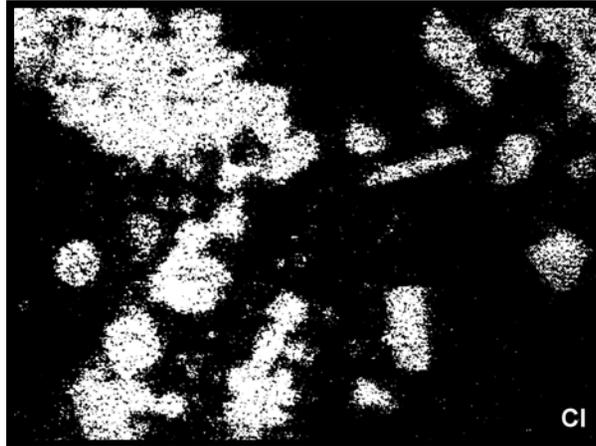
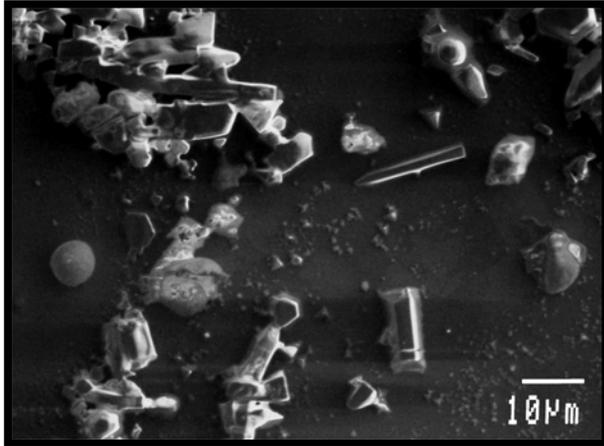
# Deliquescence and Stability of NaCl and NaCl-KNO<sub>3</sub>



- **Deliquescent NaCl is stable at 105°C (boiling point of a NaCl-saturated solution is 108.7°C)**
- **NaCl-KNO<sub>3</sub> may be transforming slowly**



# Deliquescent Brines – Deposit Formation



- Electron dispersive spectroscopy (EDS) analysis indicates precipitates contain Ca, Cl, and O
- EDS and wet-chemical analyses indicate a loss of Cl relative to Ca (HCl volatilization)
- Raman spectroscopy indicates that precipitates are not  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$
- Precipitates are possibly  $\text{CaOHCl}$



# Summary of TGA Results

- **TGA experiments conducted at controlled temperature and RH show  $\text{CaCl}_2$  transforms to non-deliquescent phases at temperatures and RH conditions of test**
- **Deliquescent  $\text{MgCl}_2$  unstable at all temperatures  $> 100^\circ\text{C}$**
- **Transformation of these salts is a result of HCl volatilization**
- **Strong temperature dependence to volatilization of HCl**
- **NaCl is stable at  $105^\circ\text{C}$**



# Volatilization of Acid Gases in the Drift Environment



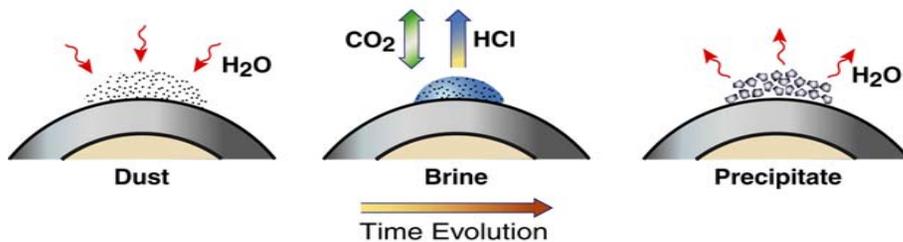
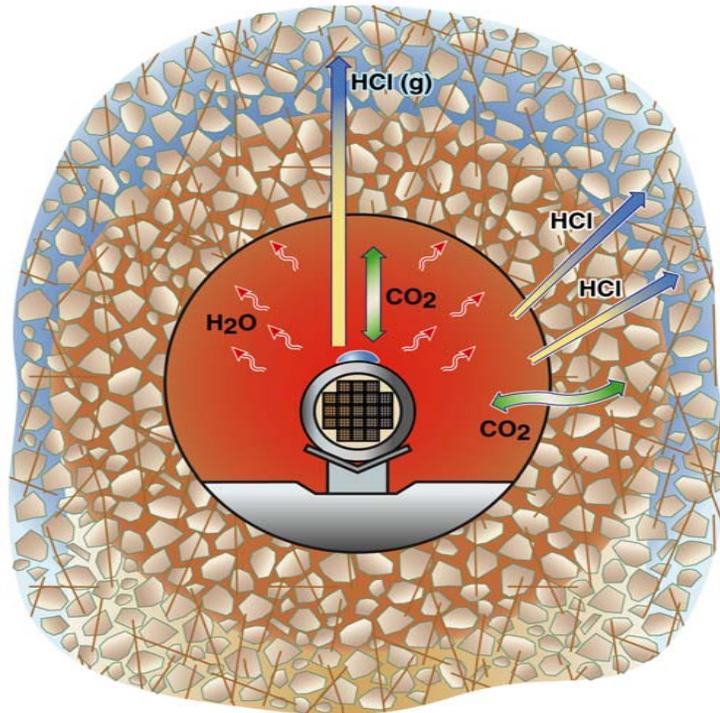
# Generation of Acid Gas in the Above-Boiling Period

- **Instability of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  (to the extent they are present) is due largely to degassing of HCl**
- **$\text{HNO}_3$  gas less volatile than HCl gas**
- **What will happen to any acid gas generated in the drift environment?**
- **How much acid gas will be generated?**



# Fate of Acid Gas in the Drift Environment

## Dust and Salt Deliquescence During the Thermal Period



NW04-008

- Under open system conditions, any HCl gas that is generated will disperse in the drift—this will occur at high temperatures when drift environment is dry
- Reactive gases will migrate along fractures in rock until encountering liquid water, where partitioning into the aqueous phase will occur
- Migration and dissolution behavior of gases in rock confirmed in the Drift-Scale Test
- Condensation will not occur on waste packages since they are the hottest spots



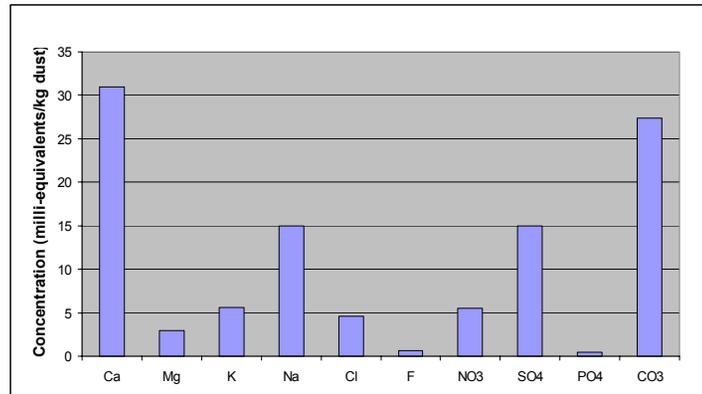
# Simulations to Demonstrate Fate of Acid Gas in the Drift Environment

Use mass of dust measured in tunnels to determine amount of dust covering a waste package



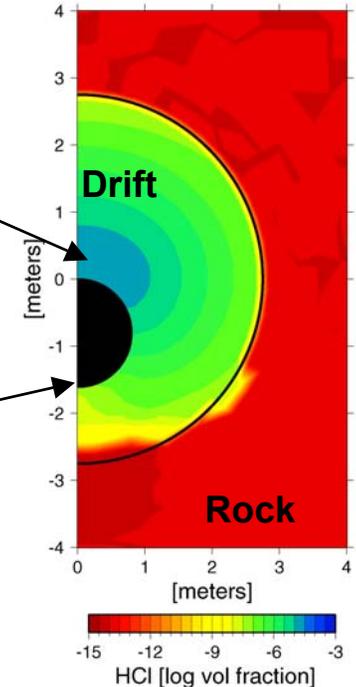
- Inject HCl gas above waste package under 2 scenarios
- 1) Drift wall just below boiling, waste package above boiling,
  - 2) Drift wall and WP below boiling, water vapor transported into drift from higher T

Use measured chloride content of dusts and assume all of the chloride volatilizes as HCl



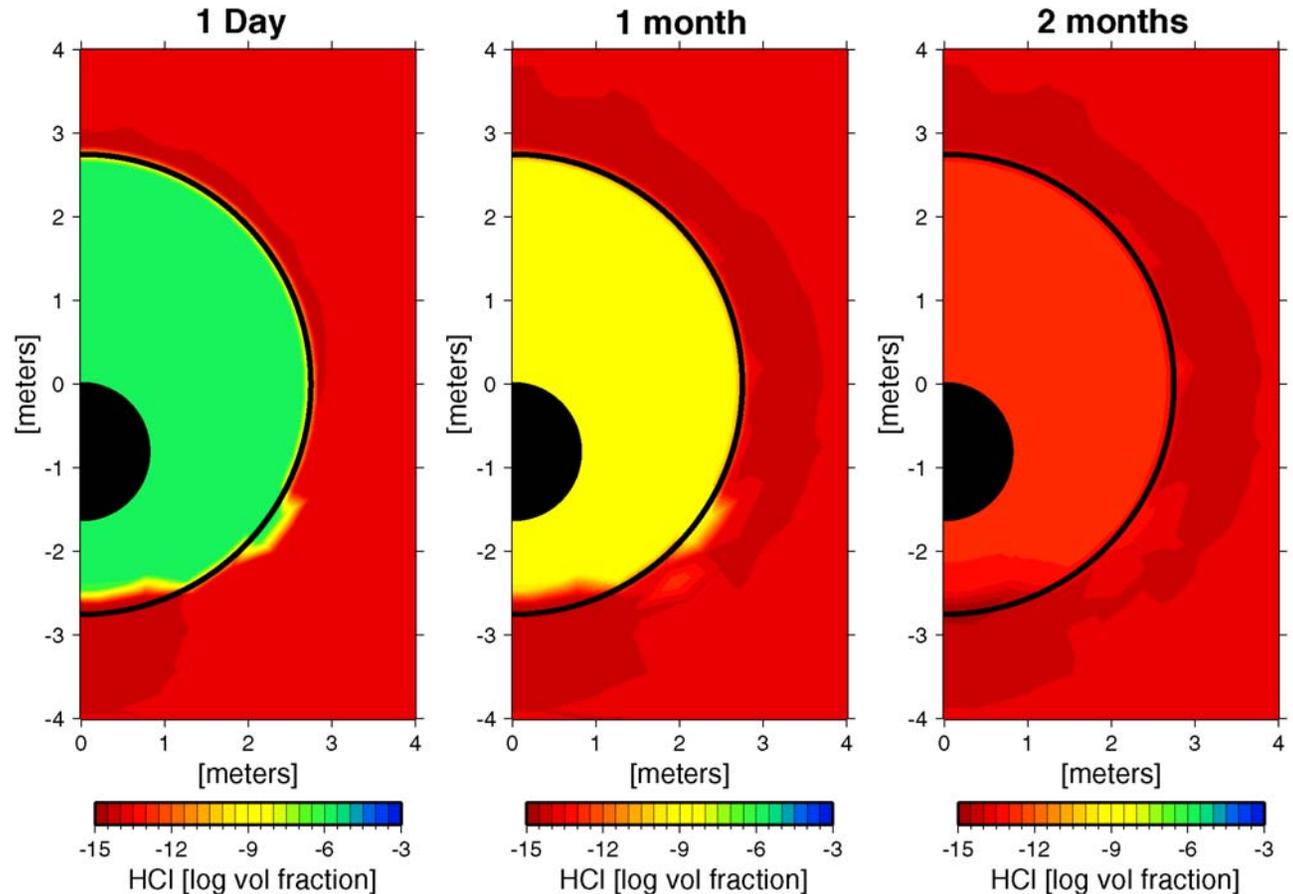
Inject HCl gas

Waste Package



# Waste Package Above Boiling, Drift Wall Below Boiling (No Condensation in Drift)

- HCl gas disperses rapidly in the drift environment
- Over slightly longer time periods, HCl gas dissolves into the aqueous phase in the rock, thus lowering its concentration in the drift atmosphere

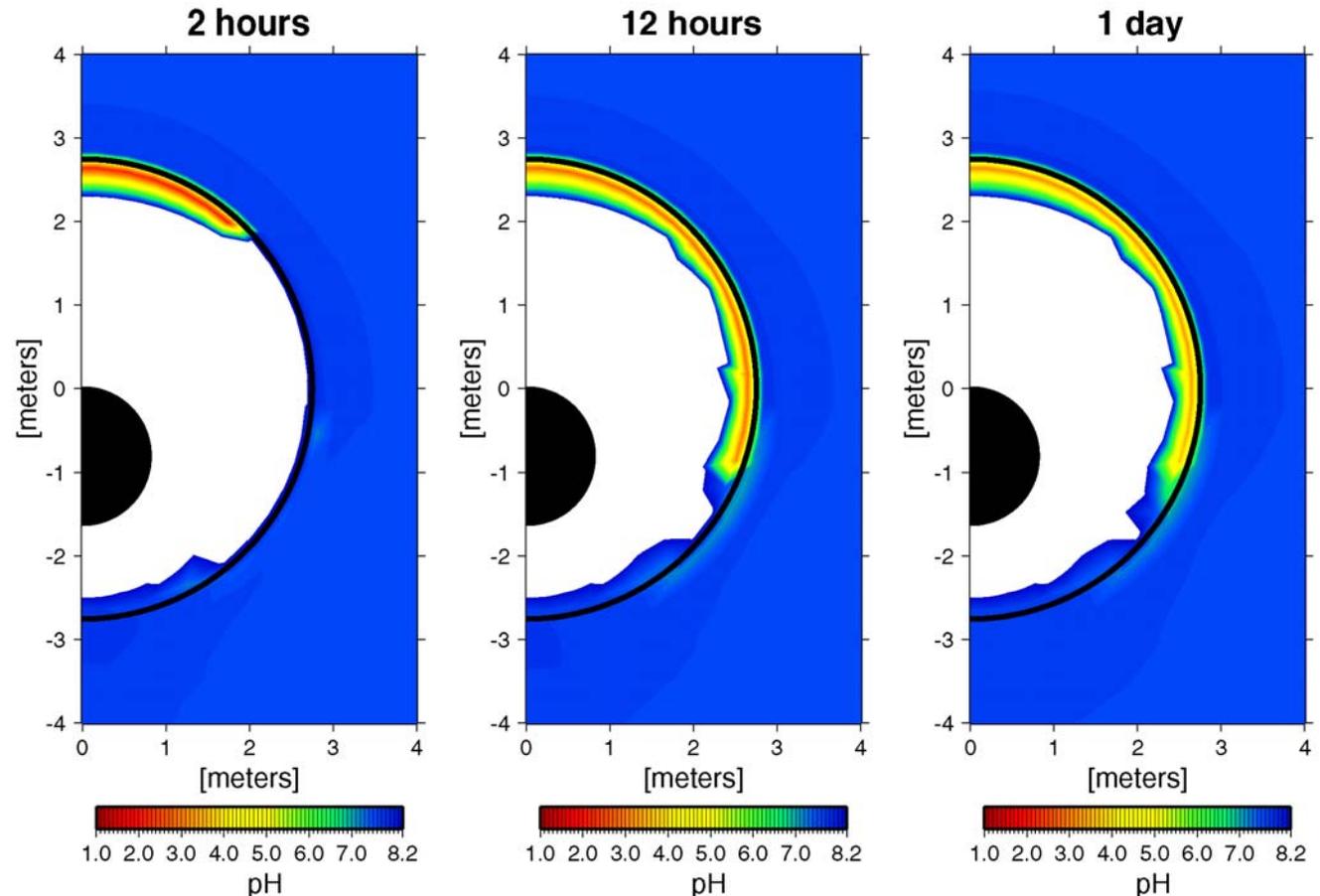


Simulations conducted at Lawrence Berkeley National Laboratory



# Drift Wall and Waste Package Below Boiling, Water Vapor Transported from Hotter Region

- When water condenses on the drift wall, its pH is lowered by the dissolution of HCl gas
- Continued water condensation raises pH with time through dilution
- No condensation of any water on waste package



Simulations conducted at Lawrence Berkeley National Laboratory



# Conclusions Concerning Acid Gases

- In the unlikely event that  $\text{CaCl}_2$  or  $\text{MgCl}_2$  are present, HCl gas can be generated during the above-boiling period
  - If this occurs, it is expected to be during the period when the entire drift temperature  $> \sim 125^\circ\text{C}$ —no condensation can occur
- Amounts of acid gas possible are small
- Any acid gases generated will be dispersed widely in the drift environment
- Upon dispersal, acid gases will dissolve into liquid water in the rock beyond the drift
- If condensation of liquid water occurs (accompanied by scavenging of HCl gas), it will take place in coolest parts of the drift (not the waste packages)



# Another Look at Salt Deliquescence

- **How much water is absorbed?**
- **What composition brines can develop?**



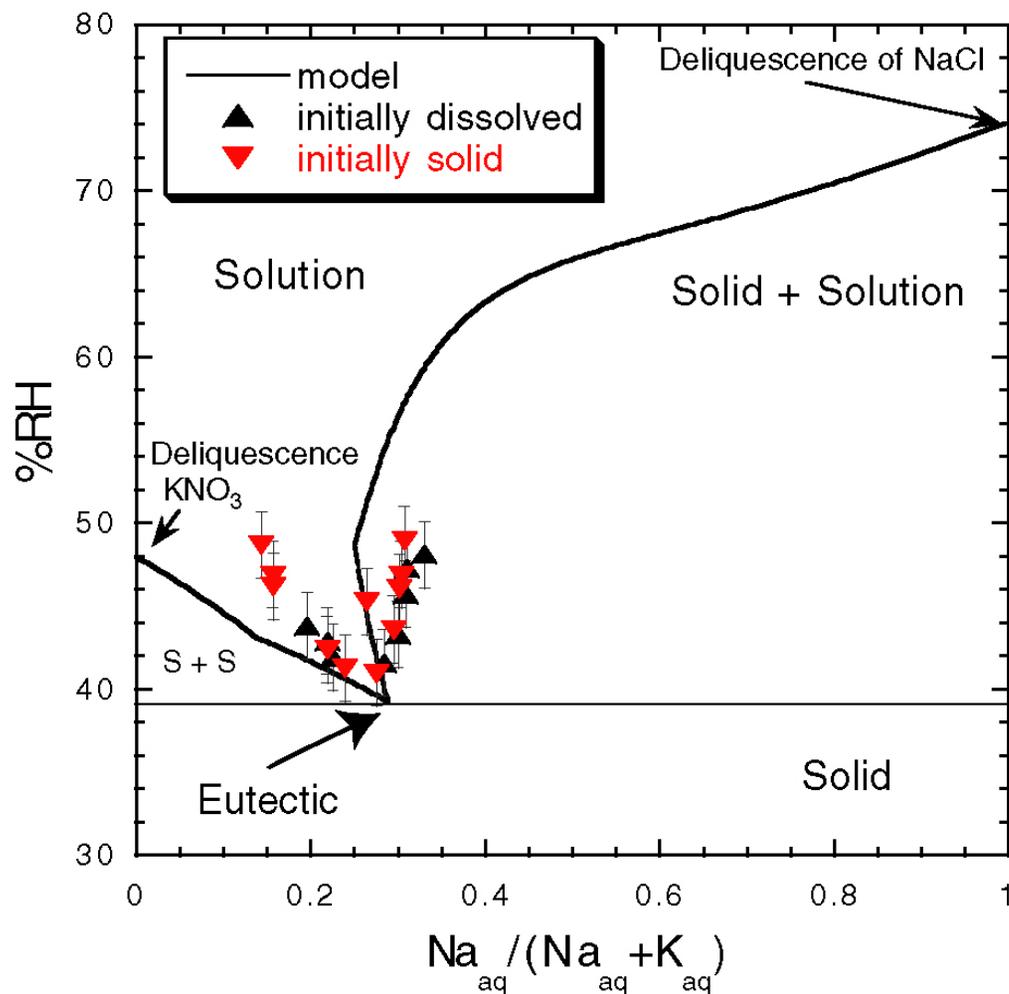
# Salt Deliquescence in Multicomponent Systems

- **Salts present in dust expected to contain both nitrate and chloride**
- **Reversed multicomponent deliquescence experiments used to validate geochemical model**
- **Mass of H<sub>2</sub>O adsorbed by deliquescent salt is very small**
- **At high temperature and low RH, eutectic composition has high NO<sub>3</sub>:Cl ratio due to thermodynamics of deliquescence**



# Validation of Geochemical Model at 120°C

- Reversed deliquescence experiments at 120°C
- Reversal occurs within about 48 hours in most cases, indicating rapid reaction rates

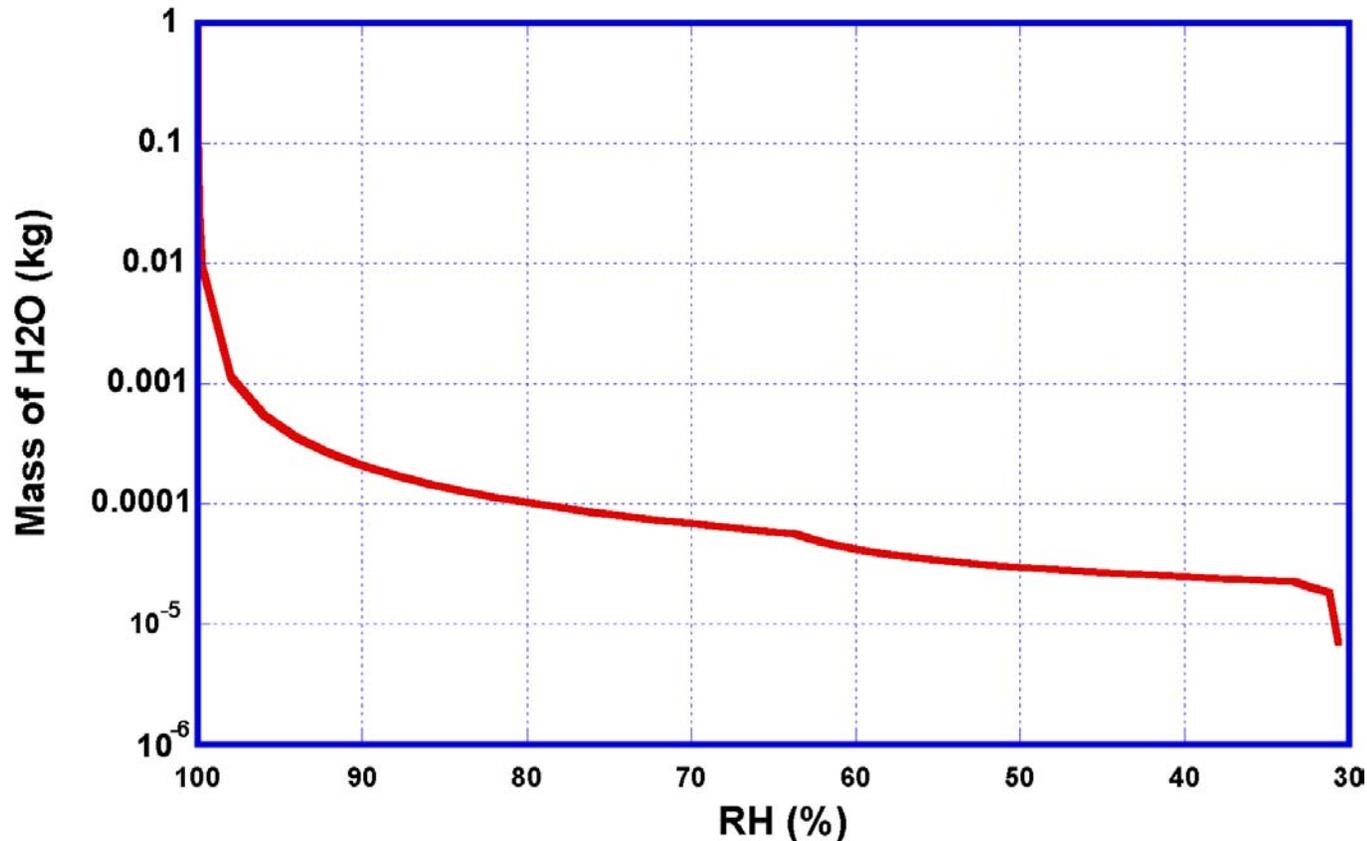


Experiments conducted at Lawrence Livermore National Laboratory



# Deliquescence in Na-K-Cl-NO<sub>3</sub> System

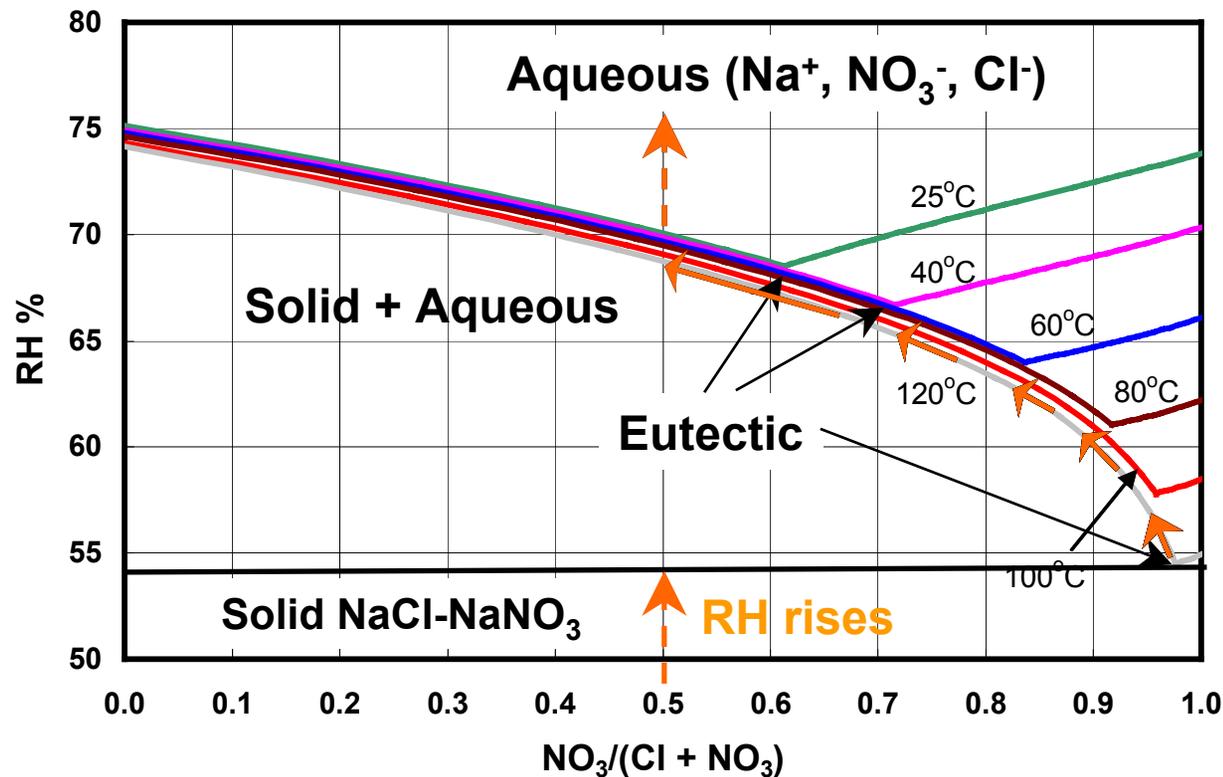
- While concentrated brines can develop due to deliquescence, brine volumes are small



For a salt mass  
of 0.35 g

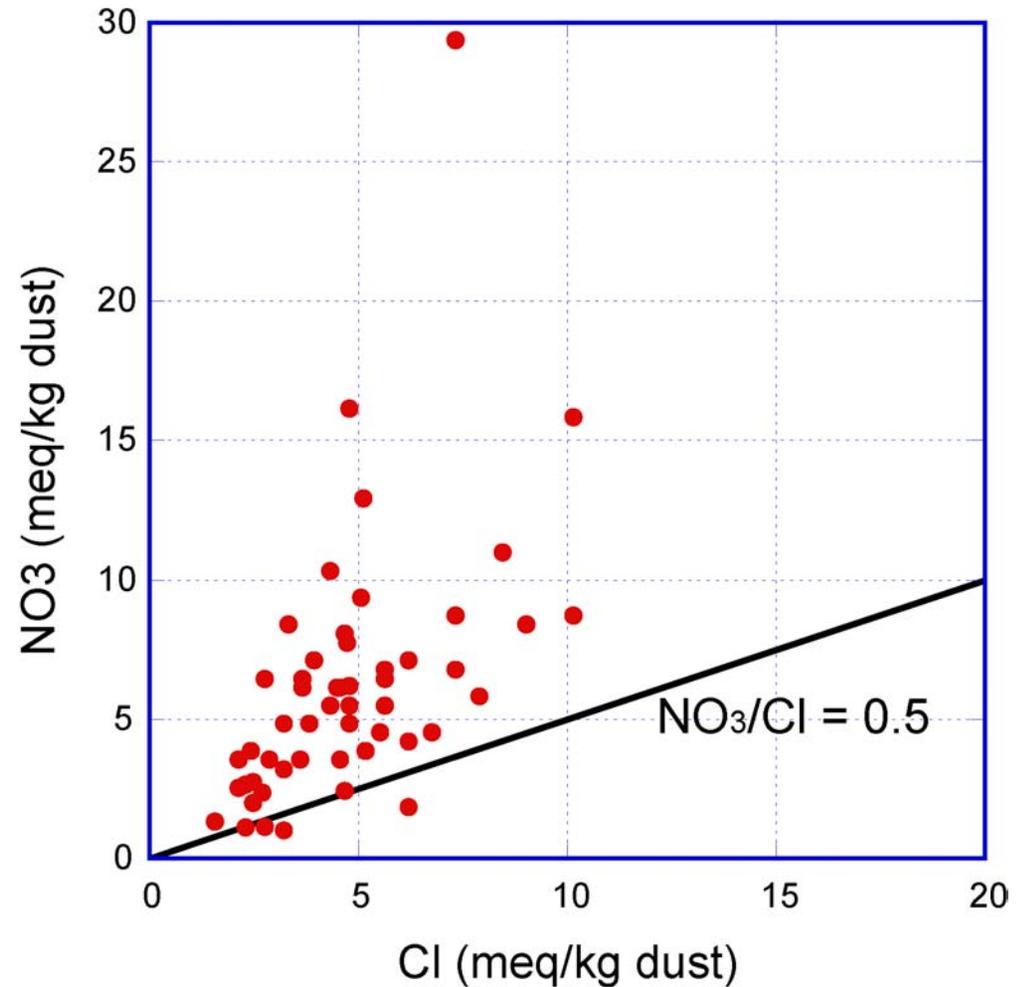


# Thermodynamic Control of $\text{NO}_3/\text{Cl}$ Ratios in $\text{NaCl-NaNO}_3$ system



# Nitrate-Chloride Ratios in Dust Leachate

- When salts dissolve completely at higher RH, solution  $\text{NO}_3/\text{Cl}$  ratios are equal to ratio in original salt assemblage
- In Na-K-Cl- $\text{NO}_3$  system, these ratios are minimum values--at lower RH, the thermodynamics of the system drive solution to higher  $\text{NO}_3/\text{Cl}$  ratios

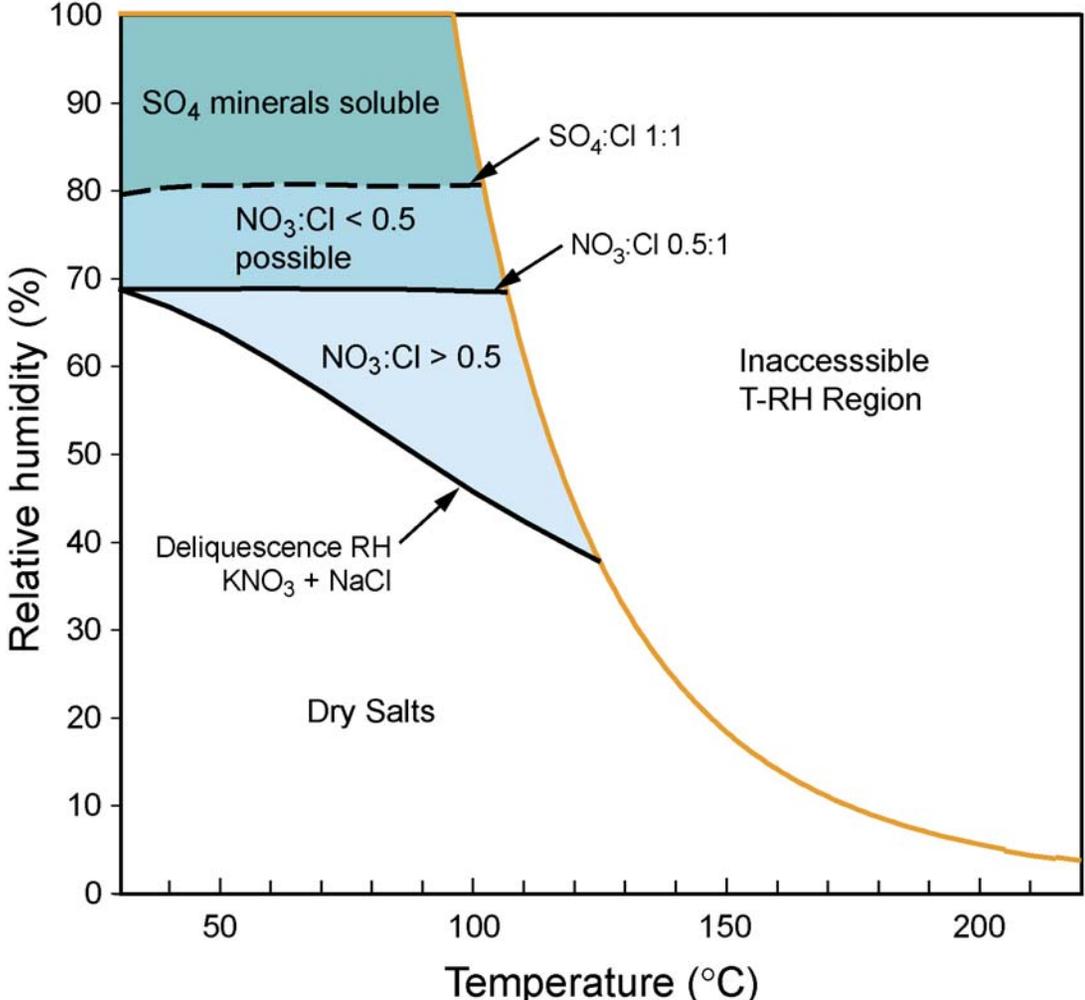


Data collected and analyzed by the United States Geological Survey



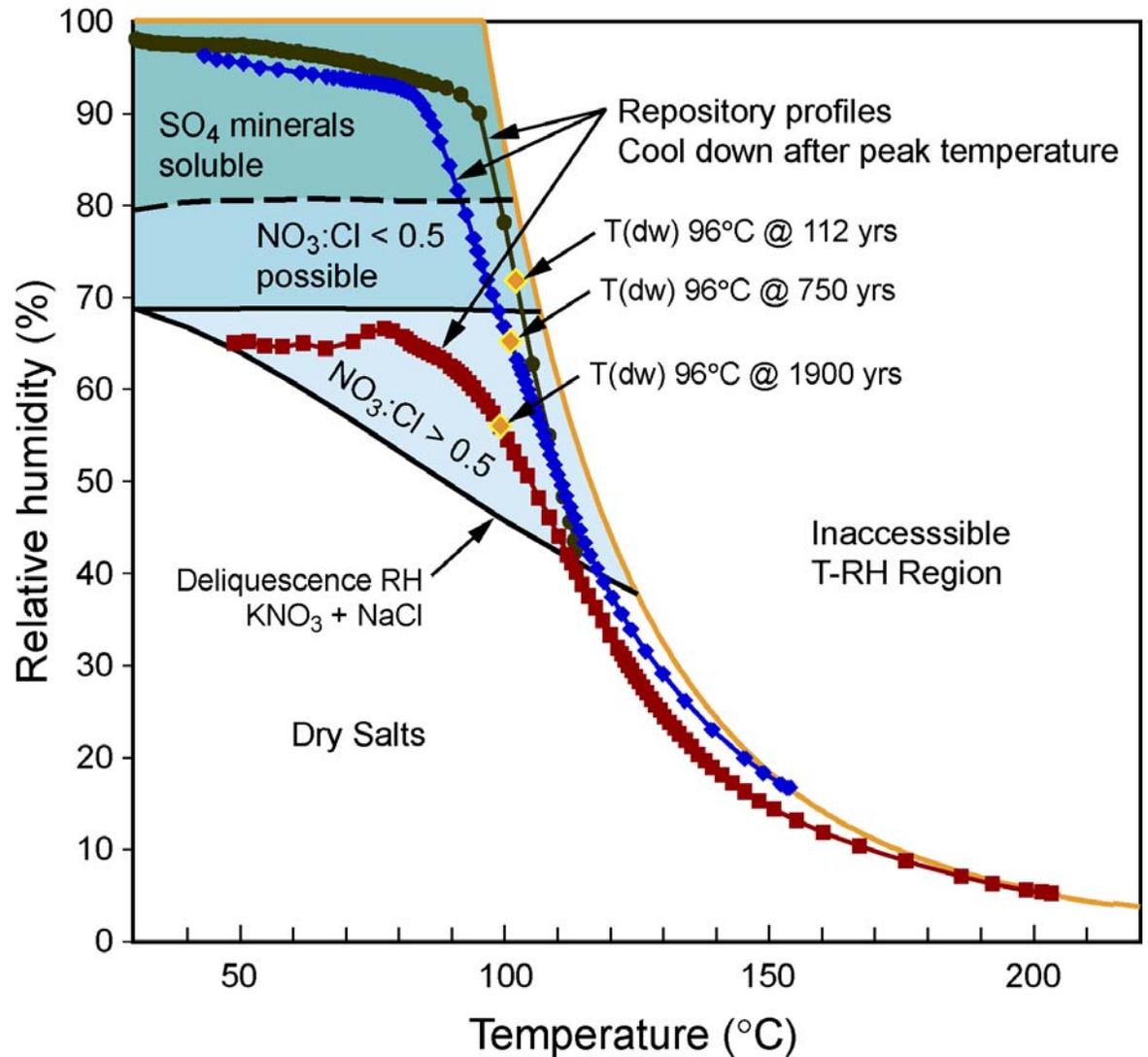
# Chemistry of Brines in Na-K-NO<sub>3</sub>-Cl System

Temperature-RH history of a waste package limits range of possible brine compositions



# Range of Possible $\text{NO}_3/\text{Cl}$ Ratios During the Above-Boiling Period

During the above-boiling period,  $\text{NO}_3/\text{Cl}$  ratios remain  $> 0.5$



# Conclusions

- Due to lack of seepage during the above-boiling period, the deliquescence of salts in dust is the chief issue
- $\text{CaCl}_2$  and  $\text{MgCl}_2$  salts are extremely unlikely to be present in the repository, but if present, will rapidly transform to non-deliquescent phases due to their instability at temperature
- Any acid gases generated due to salt deliquescence will be dispersed in drift environment and dissolved into water in the rock
- If condensation of liquid water occurs accompanied by scavenging of acid gases, it will take place in coolest parts of the drift, not on the waste packages



# Conclusions

- **Only  $\text{NO}_3^-$  dominant brines will form during the above-boiling period due to the thermodynamics of deliquescence in Na-K-Cl- $\text{NO}_3$  system**
- **Mass of  $\text{H}_2\text{O}$  taken up by salts is very small**



# Catholic University

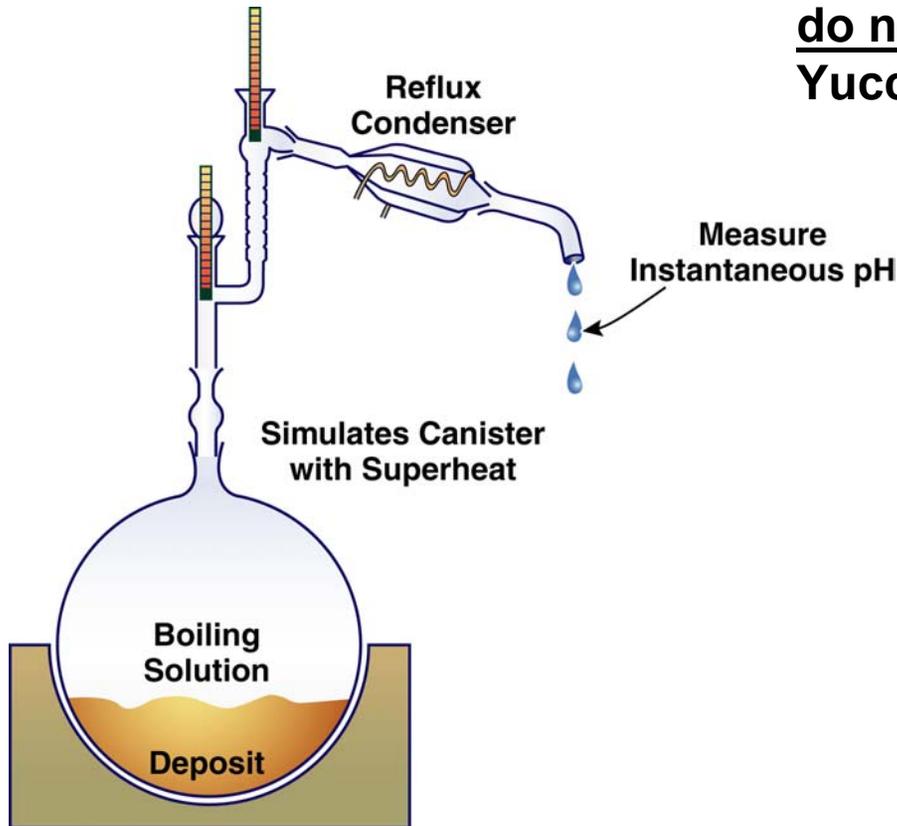
## Distillation Experiments

- **Distillation experiment involving extensive boiling of Ca-Mg-Cl-NO<sub>3</sub> water shows condensation of low pH water, leading to metal corrosion**
- **Is the experiment relevant to the drift environment?**



# Catholic University Distillation Experiment

Features of the distillation experiment that do not apply to the drift environment at Yucca Mountain



NW04-011

- Highly localized condensation due to closed system—refluxing of condensed acids back into boiling liquid
- Corroding metal coupons at lower temperature than boiling brine
- Experiment involves the equivalent of about 14,000 liters of dilute seepage water
- Very large temperature gradients

*The Catholic University distillation experiment is irrelevant to the drift environment at Yucca Mountain*



# Backup Slides



# Reactive Transport Modeling of Distillation Experiment

**ToughReact (Pitzer)  
modeling of Catholic  
University experiment  
conducted at Berkeley  
National Laboratory**

